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Measurement of the Viscosity and Density of a Reference Fluid, with Nominal Viscosity at $T = 298$ K and $p = 0.1$ MPa of 29 mPa·s, at Temperatures between (273 and 423) K and Pressures below 275 MPa

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We have measured the viscosity and density of certified reference material S20, with a nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of 29 mPa·s, at temperatures in the range of (273 to 423) K and pressures between (0.1 and 275) MPa. A vibrating wire viscometer, with a wire diameter of about 0.15 mm, was used for the viscosity measurements at pressures up to 70 MPa, and the results have an expanded uncertainty ($k = 2$) of ± 2 %, while a falling sinker viscometer was used for measurements at pressures up to 275 MPa with an expanded uncertainty ($k = 2$) of ± 2.3 %. The density was obtained from vibrating tube densimeters with an uncertainty ($k = 2$) of about ± 0.2 %. The measured viscosity and density are represented by interpolation expressions. Our equation represents the measured viscosities to within ± 2.3 % and the densities to within ±0.2 %. These differences are comparable with the expanded uncertainty ($k = 2$) of our measurements. The measurements extend the pressure range by 275 MPa and the temperature range by 50 K over which the viscosity and density of these fluids are provided by the supplier. These measurements complement those reported in the literature for S20, at pressures and temperatures exceeding the certified values, and extend the temperature range by 30 K and the upper pressure by 220 MPa. The viscosities reported here differ from values reported in the literature for batches different to that used here by less than ± 4.5 %, which is within the combined estimated expanded ($k = 2$) uncertainties of the measurements and places a plausible bound on the certainty of $\eta(T, p)$ for another batch of S20 that might be used as a calibrant for other instruments.

Introduction

The evaluation of the economics of a hydrocarbon-bearing formation requires measurements of many physical properties including both density and viscosity of the reservoir hydrocarbon. The measurements of density and viscosity are often carried out with instruments that require calibration as a function of both temperature and pressure, and calibrants are required for which the density and viscosity are known at these conditions. When a viscometer is used with conventional oil sources for which viscosity is < 100 mPa·s and density is < 904 kg·m^{-3}, at reservoir temperatures < 473 K and pressures < 210 MPa, a calibrant with similar physical properties is required. However, when the fluid is required to calibrate instruments intended to measure viscosity of other hydrocarbon reserves, for example, so-called heavy oil, the viscosity should cover the range up to ≈1000 mPa·s.[1] The uncertainty with which the viscosity and density of the calibrant are known must not exceed that required of the instruments used in the ultimate applications of the measurements. In our case, which is oil-field related, it might be acceptable to have a viscometer that was capable of determining viscosity with an expanded uncertainty of ± 10 % and density with an expanded uncertainty of ± 1 %.

The internationally agreed absolute standard for viscosity is that of water with a viscosity $\eta(H_2O$, 293.15 K, 101.325 kPa$) = (1.002 \pm 0.0025)$ mPa·s.[2,3] The viscosity and density of some pure hydrocarbons, for example, methylbenzene, are known with sufficient certainty to suffice as calibration fluids at viscosities of the order of 1 mPa·s. At viscosities up to about 121 mPa·s, Caetano et al.[4] have proposed the use of diisodecyl phthalate; the radius of their vibrating wire (with a nominal radius of 0.2 mm) viscometer[5] was determined by calibration with water at $T = 293.15$ K and $p = 101.325$ kPa and used to determine the viscosity of several fluids including certified reference material S60 with viscosities in the range of (0.5 to

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135) mPa·s with an expanded uncertainty of less than 0.6 % over this range. Several other groups are verifying the results obtained for diisodecyl phthalate, and as yet it has not been recommended by the International Association of Transport Properties (http://transp.eng.auth.gr) as a potential standard to the Bureau International des Poids et Mesures.

As an interim solution, we proposed[6,7] the continued use of other fluids, known as certified reference materials for viscosity, and we have expanded the temperature and pressure range over which the density and viscosity of these fluids have been measured. These fluids were considered by Pensado et al.[8] as possible candidates for calibration of their rolling ball viscometers. The viscosity of these substances are certified as reference materials by comparison with the viscosity of water at $T = 293.15$ K and $p = 101.325$ kPa, either directly or indirectly, through a chain of intermediate reference liquids and a series of Master capillary viscometers that establish the kinematic viscosity by the so-called "step-up" procedure to ensure the smallest possible uncertainty in calibration.[9] Unfortunately, these reference fluids must be consumed within a specified time period. In the case of petroleum-based oils, this is because the viscosity increases, presumably through evaporation of lower molar mass components, at a rate that varies from (0.01 to 0.03) % per month.

Lundstrom et al.[6] and Sopkow et al.[7] determined the viscosity of certified reference materials N10 and S20 over the range of (1.8 to 76) mPa·s at temperatures between (298 and 353) K and pressures below 55 MPa, for which neither the supplier nor the literature provides values. In refs 6 and 7, a vibrating wire viscometer with a nominal wire diameter of 0.1 mm was used, and the density reported in ref 6 was measured with an oscillating tube densimeter. These results were combined with the values of density and viscosity provided by the supplier at $p = 0.1$ MPa to obtain interpolation expressions for both properties with leading terms based on the cited values. In view of the reported international consistency of these fluids,[10] it was speculated that adopting this formalism might allow small differences between the cited values to be accommodated by solely substituting values obtained from either other lots of the same supplier or an alternative supplier of certified reference material N10 and S20.

In this work, we have used a vibrating wire viscometer, with a wire diameter of 0.15 mm, and a falling sinker viscometer[11] to measure the viscosity of certified reference material S20 with nominal viscosity of 29 mPa·s at $T = 298$ K and $p = 0.1$ MPa at temperatures between (273 and 423) K at pressures below 275 MPa. Our measured viscosities covered the range of (1.4 to 80) mPa·s for the vibrating wire and (5.5 to 1280) mPa·s for the falling sinker. The sample of S20 used in this work was from a different batch than used in refs 6 and 7. These measurements extend the upper pressure at which the viscosity has been measured by 220 MPa. In this work, we also used a vibrating U-tube densimeter to determine the density of the certified reference materials at temperatures between (273 and 423) K at pressures below 70 MPa; the density must be known with an uncertainty of the order of 1 % to obtain viscosity from measurements of the time taken for a sinker to fall a known distance.

Working Equations

Vibrating Wire Viscometer. For Newtonian fluids, the vibrating wire has exact working equations that have been fully described in refs 12 to 19. The equations used have been reported, and the interested reader is referred to, for example, eqs 1 through 9 of our previous work.[20] Our vibrating wire viscometer comprises a thin metallic wire clamped under tension between two fixed supports and immersed in the fluid. The wire is placed in a magnetic field and driven in steady-state transverse oscillations by passing an alternating current through it. The viscosity of a fluid of known density is adjusted in a regression until the in-phase and quadrature voltages determined from the working equations are consistent with the experimental values over the resonance frequency. If a mass is suspended from the lower end of the wire, the wire tension varies according to Archimedes principle. Density can also be obtained by modification of the working equations.[21]

The vibrating wire viscometer is an absolute device that, in theory, requires no calibration constants to be determined. The hydrodynamic model includes the resonance frequency in the absence of fluid and damping, the internal damping of the wire in vacuum, the wire radius, and the wire density. When these parameters are known along with the density of the fluid sample, the viscosity of the fluid can be obtained from the width of the resonance curve. However, in practice the wire damping factor and radius cannot be determined to sufficient accuracy by independent methods, and those values are usually determined by calibration. To do this, measurements are made in both vacuum and a fluid for which the viscosity and density are known. The former yields the damping factor Δ_0. The wire radius, R, can be determined from a single measurement when immersed in, typically, methylbenzene[22] but ideally water as demonstrated by Caetano et al.[5] In this work, we have not determined the vacuum frequency; it is an adjustable parameter in the analysis.

Falling Body Viscometer. The working equations for the falling body viscometer, which has been described in detail in refs 11, 23, 24, 25, and 26 (for example, eq 1 of ref 24), require measurement of the time a sinker takes to fall a known distance and knowledge of the densities of the fluid and the material from which the sinker was formed. The analysis also requires values for the linear thermal expansion coefficient and the bulk compressibility of the sinker and tube materials. A constant of calibration is also required that we defer discussion of for the Apparatus and Experimental Procedure section. In this analysis, it is assumed that the sinker reaches terminal velocity prior to determining the time required to fall a known distance. According to Harlow,[27] the distance travelled by a sinker to reach terminal velocity is proportional to the sixth power of the clearance between the inner radius of the viscometer tube and the outer diameter of the sinker.

The sinker is a hollow cylinder with a hemispherical end containing a ferrite core. The sinker falls unguided and may not be self-centering and thus could fall eccentrically. The effect of eccentric fall is to reduce the flow time[28] as also happens with turbulent flow. Under these conditions, measurements are best made within upper and lower Reynolds number limits where the calibration factor A is constant.

Vibrating Tube Densimeter. For a vibrating tube densimeter, Retsina et al.[12] reported a working equation for a straight tube clamped at both ends and filled with fluid and surrounded by either another fluid or vacuum; this analysis assumes that the fluid within the tube does not flow and thus the viscosity of the fluid is neglected. If negligible internal damping is assumed, then the expression has been derived by Retsina et al.[12] (eq 3 of ref 6), which is the working equation routinely used for vibrating U-tubes.[29−32] It applies even when the cross section is non-uniform and the tube is curved into a U.[31] The two calibration constants are determined through calibrations with two reference liquids of known density, such as water and methylbenzene, or with one liquid of known density, for example, water, and with either vacuum or a dilute gas. Typically, the calibration is performed with fluids that have $\eta < 1$ mPa·s. Bernhardt and Pauly[33] and Ashcroft et al.[34] have determined the error arising from neglecting viscosity in the working equations by comparing the results obtained with the vibrating tube with values determined with a pycnometer: Bernhardt and Pauly[33] considered fluids with viscosities in the range (1 to 10^3) mPa·s (with an Anton Paar DMA 02C densimeter) while Ashcroft et al.[34] studied fluids with viscosities between (1 and 40) mPa·s with a glass U-tube (Anton Paar model DMA 602). Both refs 33 and 34 determined that the vibrating tube gave values greater than the pycnometer and provided empirical expressions as a function of viscosity to estimate the correction. Anton Paar[35] recommend for a model 512P densimeter (similar to that used by us and described in the section below) for $\eta < 100$ mPa·s the correction to density for fluid viscosity of

$$\Delta\rho = \rho[-0.5 + 0.45(\eta/\mathrm{mPa{\cdot}s})^{1/2}]\cdot 10^{-4} \qquad (1)$$

that is subtracted from the measured density. For a vibrating tube filled with fluid of $\eta \approx 80$ mPa·s, the worst case in our experiment, eq 1 returns $\Delta\rho/\rho = 0.035$ % while extrapolation of the expression reported in ref 33 by about 30 mPa·s gives $\rho/\rho = 0.044$ % and that of ref 34 provides $\Delta\rho/\rho = 0.048$ %. However, it still remains a task for theoretical mechanics to explain this observation.

Apparatus and Experimental Procedure

Vibrating Wire Viscometer. The vibrating wire viscometer was described by us previously,[20] and only the important features are provided here. It was formed from tungsten wire of length about 40 mm with a nominal radius of about 0.075 mm obtained from Goodfellow, Cambridge, U.K., with a mass fraction purity > 99.95 %. The wire was cold drawn, and consequently, the cross-section had elliptical rather than circular symmetry, which results in the resonance appearing as a doublet. The magnetic field was aligned so as to preferentially excite one of the two components arising from non-circular symmetry. The two clamps were separated from each other by a tube fabricated from MACOR (machinable glass ceramic) obtained from Wesgo Ceramics, Hayward, U.S. The electrical resistivity of this material is $> 10^{16}$ Ω·m, and the linear thermal expansion coefficient $\approx 1.3\cdot 10^{-5}$ K^{-1}, which is about 4 times that of tungsten at $T = 298$ K. For operation at temperatures up to 423 K, the different thermal expansion coefficients of MACOR and tungsten gave rise to an increased wire tension and thus resonance frequency. However, on the basis of the measurements reported in ref 20, no detrimental effects were observed for the performance of the vibrating wire as a viscometer. The ceramic tube had an inner diameter of 7.5 mm so that for the wire of 0.15 mm diameter the ratio of the former to the latter diameter is 50. Thus our design complies with an assumption used to obtain the working equations, namely, that the ratio of the inner radius of the body containing the fluid to that of the wire is greater than 45 for Reynolds numbers < 100.[12,13]

The magnetic field was provided by two rectangular magnets of 31 mm length located symmetrically along the length of the wire so as to suppress the second and third harmonics. The magnetic field was exposed to the fluid and exerted a field of about 0.3 T on the wire, so the largest force applied at a current of 1.2 mA was about 10^{-5} N.

The assembled vibrating wire was placed in a pressure vessel with a maximum operating pressure of up to 70 MPa at the highest operating temperature. The fluid flowed into and out of the apparatus through two ports located at the bottom and top of the vessel, respectively. The vessel was placed in a stirred-fluid bath (Julabo, model FK31-ME) whose temperature was controlled with a precision of ± 0.01 K.

The temperature of the vibrating wire viscometer pressure vessel and the high-pressure vibrating tube densimeter were determined with a four-wire industrial grade platinum resistance thermometer with a nominal resistance of 100 Ω. This thermometer had been calibrated against a standard 25 Ω platinum resistance thermometer that had itself been calibrated on the ITS-90. The resistance was determined with a multimeter and converted to temperature with an uncertainty, including the calibration, of about ± 0.01 K.

Pressure was generated with a hydraulic pump and measured, in the range of (10 to 70) MPa with a dial gauge (Heise, Stratford, CT, model CM12524) with a resolution of 0.1 MPa and uncertainty specified as ± 0.25 MPa. This uncertainty was confirmed by calibration against a force balance dead-weight gauge (Desgranges et Huot model 21000) with an uncertainty of ± 0.05 MPa. On the basis of the viscosity of S20 reported by Lundstrom et al.,[6] we estimated the $\delta p \approx 0.25$ MPa contributes, at most, an additional uncertainty in viscosity of up to 0.7 %.

The voltage of the sinusoidal signal generated by a lock-in amplifier (with a maximum output of 5 V ac) and the variable resistance (maximum value of 1 kΩ connected in series with the tungsten wire) were adjusted to maintain the estimated amplitude of the wire motion less than 10 % of its radius. For the $R \approx 0.075$ mm at $\eta \approx 1.4$ mPa·s, $I \approx 0.2$ mA while for $\eta \approx 45$ mPa·s, $I \approx 1.2$ mA.

The tungsten wire $\{c_p(\mathrm{W}, 298\ \mathrm{K}) \approx 0.133\ \mathrm{kJ\cdot kg^{-1}\cdot K^{-1}}$ and $\rho(\mathrm{W}, 298\ \mathrm{K}) \approx 19\,300\ \mathrm{kg\cdot m^{-3}}\}$ of $R \approx 0.075$ mm and mass $1.4\cdot 10^{-5}$ kg has a resistance of order 1 Ω. When it was immersed in S20 $\{c_p(298\ \mathrm{K}) \approx 2\ \mathrm{kJ\cdot kg^{-1}\cdot K^{-1}}$, $\rho(298\ \mathrm{K}) \approx 840\ \mathrm{kg\cdot m^{-3}}$, and $\kappa \approx 120\ \mathrm{mW\cdot m^{-1}\cdot K^{-1}}\}$, with the highest current of 1.2 mA, over the 200 s acquisition time the fluid temperature was estimated to rise by 0.1 mK {assuming all electrical energy dissipated into the fluid volume enclosed by the wire holder (about $2\cdot 10^{-6}$ m^3)} and the resulting worst case error in viscosity at $T = 298$ K and $p = 50$ MPa, where $\eta = 80$ mPa·s and $\mathrm{d}\eta/\mathrm{d}T \approx -1.24$ mPa·s·K^{-1}, would be ≈ 0.0002 %. The temperature rise resulting from the wire motion within the fluid was always negligible.

The frequency generated by the synthesizer was stepped over the resonance frequency of the wire and the in-phase and quadrature voltages, which included the motional emf, were determined with the lock-in amplifier over the frequency range ($f_\mathrm{r} \pm 5g$), where g is half the resonance line width at a frequency 0.707 times that of the maximum amplitude and f_r is the fundamental transverse resonance frequency; over ranges of viscosity, density, temperature, and pressures of these experiments f_r varied from (1192 to 2055) Hz with the lowest frequency observed at the highest viscosity. The frequency sweep started at ($f_\mathrm{r} - 5g$) with positive frequency steps to ($f_\mathrm{r} + 5g$) and then with negative increments to ($f_\mathrm{r} - 5g$) and took about 200 s for acquisition. The temperature was measured at each acquisition frequency and then averaged.

Prior to acquiring the complex voltages, the majority of the contribution arising from the drive voltage was removed by setting the lock-in offset voltage at $f < (f_\mathrm{r} - 5g)$. However, the scan range depended on the quality factor $Q\ \{= f/(2g)\}$ of the wire resonance. The Q decreased from 50.9 for η (S20, 423 K, 0.1 MPa) ≈ 1.4 mPa·s to 3.3 for η (S20, 298 K, 50 MPa) ≈ 80 mPa·s. At a constant drive current as the viscosity increases there is also a corresponding decrease in signal-to-noise ratio.

For each fluid temperature and pressure, the measured complex voltage was replicated by adjusting a, b, and c of eq 2, f_0 of eq 3, and η of eq 9 of ref 20 using R and Δ_0 from the calibration and the appropriate density. This numerical procedure separates the complex voltages arising from the background and the motion utilizing the different frequency dependence of eqs 2 and 3 of ref 20, respectively. The fluid density was obtained from a modified Tait equation[36] (see eqs 4 and 5 of ref 6), with coefficients adjusted to represent our measurements, and is described in the Results and Discussion section.

Measurements of complex voltage in vacuum were used to obtain Δ_0, while measurements in methylbenzene at a temperature of 298.15 K and pressure of 0.1 MPa were used to obtain the radius R using the viscosity and density of methylbenzene recommended by Santos et al.[37] These measurements gave $R = 0.0716$ mm and $\Delta_0 = 12.2 \cdot 10^{-5}$.

The uncertainty in our measurements of viscosity have, based on the measurements reported elsewhere in refs 6, 7, and 20, an estimated expanded uncertainty of ± 2 %. The uncertainty in R dominates the uncertainty in η but for liquids the working equations are insensitive to the value of Δ_0, and there is no requirement to determine this parameter with high precision. We did not include corrections to both the wire radius and density of the wire that account for variations in temperature and pressure. It has been reported that these amount to an additional uncertainty in viscosity of less than 0.1 %.[21]

The values of f_0, the frequency of the wire in the absence of fluid and internal damping, determined from the regression analysis (to eq 3 of ref 20) gave $\mathrm{d}f_0/\mathrm{d}T$ of between (0.2 and 0.3) Hz·K^{-1} over the temperature range of (298 to 423) K. These variations are in the range anticipated solely from the variation in wire tension that would arise from the difference in the linear thermal expansion coefficients between tungsten and MACOR. However, we also found that f_0 decreased linearly with increasing pressure with $\mathrm{d}f_0/\mathrm{d}p$ in the range ≈ −8 Hz·MPa^{-1} at $T = 298$ K to ≈ −5 Hz·MPa^{-1} at $T = 423$ K. We have not performed experiments to identify the source of this observed variation; plausible sources include variations in wire tension and the length and rotation of one wire clamp relative to the other. According to the working equations,[20] f_0 is specific to the particular end condition chosen for the wire. In practice, it is impossible to know the end conditions for the wire exactly so that any applied condition will yield only a good approximation to the true f_0. Thus, to accurately determine viscosity we allowed f_0 to float in the regression analysis. Had we fixed f_0 in the analysis to a value determined at $p = 0$ for each temperature, the viscosity determined would include a systematic error that Lundstrom et al.[6] reported can be up to 50 %.

Falling Sinker Viscometer. The high-pressure falling sinker viscometer and its operation have been described in detail elsewhere,[23,24] and only the important features are described here. The falling body viscometer consists of a tube and sinker with a fixed clearance between the two parts. The movement of the sinker, which contained a magnet, was determined with two coils positioned outside the tube and a known distance apart. These coils were used to determine the fall time. In our viscometer, the tube has an internal diameter of 6.52 mm. Because of the wide range of viscosity encountered for S20 {≈ (5.2 to 1280) mPa·s, a factor of 246} and the requirement to both reach terminal velocity and have a finite t, two sinkers of different r, and thus different clearance from the inner surface of the tube, were used. These had nominal diameters of (6.0 and 6.3) mm. Decreasing the diameter of the sinker allows operation with higher viscosity fluids. The sinker densities were corrected for changes in T (and p) from the reference state of $T_{\mathrm{ref}} = 298.15$ K and $p_{\mathrm{ref}} = 0.1$ MPa.[23,24] Both sinkers and the tube were constructed from $\{0.6585\mathrm{Fe} + 0.0008\mathrm{C} + 0.02\mathrm{Mn} + 0.00045\mathrm{P} + 0.0003\mathrm{S} + 0.01\mathrm{Si} + 0.17\mathrm{Cr} + 0.12\mathrm{Ni} + 0.02\mathrm{Mo}\}$, commonly known as type 316 stainless steel, so that $\rho_{\mathrm{S}} \approx 8000$ kg·m^{-3}, $\alpha \approx 1.6 \cdot 10^{-5}$ K^{-1}, and $\beta \approx 2 \cdot 10^{-6}$ Pa^{-1} of eq 1 of ref 24.

To determine the calibration parameter A (eq 1 of ref 24) the method of calibration was changed from the approach frequently used for a falling sinker viscometer, which relies on a correlation for the viscosity of methylbenzene at $p = 0.1$ MPa.[37] For this work, a different strategy was adopted that utilized a set of certified reference fluids for viscosity as the calibrants over the temperature range (293 to 323) K.[38] The certified reference materials for viscosity (obtained from the Cannon Instrument Co., State College, PA) were N100, S200, and N1000 (with lot numbers 03501, 04201, and 05201, respectively). Analysis of the measured sinker fall times in these fluids, of known and certified density and viscosity, gave A(6.0 mm) = (2.474 ± 0.009) Pa^{-1} (with standard uncertainty) that covers the viscosity range (51 to 2875) mPa·s and A(6.3 mm) = (28.72 ± 0.07) Pa^{-1}. When the expanded uncertainties in replicate measurements (± 1 %), the uncertainty in the viscosity of the calibration fluids of ± 0.35 % and reproducibility of the calibration measurements of ± 2 % are combined in quadrature, and expanded uncertainty in the viscosity measurements is estimated to be ± 2.3 %.

Calculation of the viscosity from the measured sinker fall time (eq 1 of ref 24) requires the fluid density. This could be obtained by extrapolation of our measurements at pressure up to 70 MPa with a modified Tait equation[36] (see eqs 4 and 5 of ref 6) to pressures of 300 MPa or adopting the procedures used for the falling sinker viscometer previously.[24,38] Both methods of estimating the density are described in the Results and Discussion section. Fortunately, to obtain viscosity from eq 1 of ref 24 requires knowledge of the density with an uncertainty of about 5 % because the density of the sinker is about 8 times that of S20 and enters the calculation as a buoyancy factor $(1 - \rho/\rho_{\mathrm{s}})$. The densities required for the calculation are described in the Results and Discussion section and have an expanded uncertainty of less than ± 0.2 %, which is more than sufficient for the determination of viscosity from the falling sinker.

The viscometer was immersed in a stirred-fluid thermostat (filled with Shell Diala B), and the temperature was maintained constant by a combination of a heater controlled with an on−off controller and a bridge circuit employing a thermistor as one arm and refrigerated ethanol circulated through a heat exchanger. The temperature was measured with a platinum resistance thermometer calibrated at temperatures between (208 and 373) K on ITS-90 with an uncertainty of ± 0.01 K. The oil-bath temperature was controlled within ± 0.01 K.

Pressures below 400 MPa were measured with a dial gauge (Heise CM, Dresser Instruments, Stratford, CT), which when calibrated against an oil lubricated dead-weight gauge was found to have an expanded uncertainty of ± 0.05 % of full scale (about 0.2 MPa at $p = 400$ MPa). After each measurement of the sinker fall time, the viscometer pressure vessel was inverted by a stepper motor to return the sinker to the starting position. The viscosity was obtained along an isotherm with the following procedure: (1) replicate (usually three) measurements were obtained at a temperature and atmospheric pressure; (2) the pressure within the viscometer was increased manually to a pressure just above the maximum operating value; (3) the pressure was adjusted automatically to the highest of a set of pressures by moving the piston of a positive displacement pump (model 37-5.75−60, High Pressure Equipment Co., Erie, PA) connected to the viscometer pressure vessel and kept at ambient temperature, while the pressure was monitored by a transducer (Wika model 891.01.2002, Alexander Wiegand GmbH & Co., Klingenberg am Main, Germany); (4) after a time interval sufficient to achieve thermal and hydrostatic equilibria replicate (again usually three) sinker fall times were measured; and (5) the process (2) through (4) was repeated for each predetermined pressure down to $p = 0.1$ MPa.

Vibrating Tube Densimeters. For both the vibrating wire (clamped at both ends) and falling sinker viscometers, measurements of the density are required to determine viscosity from the observations with the working equations. The density of S20 was determined with two vibrating U-tube densimeters: one capable of operating at pressures up to 70 MPa (an Anton Parr model 512) and the other for measurements at $p = 0.1$ MPa (Anton Paar DMA5000).

Prior to performing measurements with S20, the constants of the high-pressure densimeter were obtained by calibration using methylbenzene and water (which was degassed by boiling while maintained at $p \leq 10$ Pa) at temperatures in the range of (298 to 423) K and pressures below 70 MPa. The densities of these two calibrants cover the range of values expected for S20. The values for methylbenzene were taken from the correlations reported by Assael et al.,[39] and the values for water were taken from those of Wagner and Pruss.[40] On the basis of the trends of the constants as a function of temperature and pressure, we conclude that the U-tube densimeter has an expanded uncertainty of ± 0.2 %.

The temperature of the high-pressure vibrating tube densimeter was determined with the four-wire industrial grade platinum resistance thermometer on ITS-90 with an uncertainty, including the calibration, of about ± 0.01 K. The temperature of the stirred-fluid thermostat was controlled with a precision better than ± 0.1 K, and this, worst case, uncertainty in temperature contributes less than ± 0.01 % to the estimated uncertainty in density. An uncertainty of ± 0.1 % in the density yields an uncertainty of ± 0.05 % in the viscosity determined from the vibrating wire.[5]

The low-pressure densimeter, which had an integral thermometer, was operated at temperatures in the range (273 to 363) K. The manufacturer cited an uncertainty for temperature of ± 0.01 K and density of $\pm\ 0.005\ \text{kg}\cdot\text{m}^{-3}$ for densities less than $3000\ \text{kg}\cdot\text{m}^{-3}$ and pressures below 1 MPa; the cited repeatability for density was $0.001\ \text{kg}\cdot\text{m}^{-3}$. Prior to performing measurements with S20, the densimeter calibration was verified with measurements on dry air (BOC Gases Instrument Grade, $25\cdot10^{-6}$ volume fraction water) and water (purified with an ion-exchange column) at temperatures of (293, 313, and 333) K. Our results were compared with values obtained by combining the measured temperature and pressure with correlations reported by Davis[41] for air and by Wagner and Pruss[40] for water. For air, the density obtained from ref 41 differed insignificantly from that determined with the equation of state reported by Lemmon et al.[42] Our results differed insignificantly from the literature correlations. The measured densities were corrected for sample viscosities using the in-built viscosity correction for this instrument. The validity of this correction was confirmed with measurements of the density of certified reference fluids S200 and N4000, supplied by Cannon Instruments, USA, with viscosities in the range of (0.5848 and 16.17) Pa·s at $T = 293$ K and $p = 0.1$ MPa.[38] The density and viscosity of these fluids were measured by the supplier according to ASTM D 2164 and ASTM D 1480, respectively, over the temperature range of (293 and 373) K and given uncertainties of ± 0.25 % in viscosity relative to water at $T = 293$ K and ± 0.02 % for density. On the basis of these measurements, we conclude that the U-tube densimeter has an uncertainty of $\pm\ 0.05\ \text{kg}\cdot\text{m}^{-3}$, 10 times that cited by the manufacturer. The densimeter was cleaned with filtered ethanol, acetone, and dry air prior to determining the density of each fluid.

Table 1. Viscosity η and Density ρ Provided by the Manufacturer for Certified Reference Material S20 at Temperature T and $p = 0.1$ MPa with Estimated Expanded Uncertainties

T/K	ρ/kg·m^{-3}	η/mPa·s
293.15	862.30 ± 0.17	37.67 ± 0.13
298.15	859.10 ± 0.17	29.33 ± 0.10
310.93	850.80 ± 0.17	16.790 ± 0.059
313.15	849.40 ± 0.17	15.380 ± 0.054
323.15	843.00 ± 0.17	10.740 ± 0.038
353.15	823.70 ± 0.16	4.632 ± 0.016
372.04	811.60 ± 0.16	3.107 ± 0.011
373.15	810.80 ± 0.16	3.043 ± 0.011

Materials and Measurements. The certified reference materials for viscosity S20 {with nominal viscosity of about 29 mPa·s at $T = 298$ K and $p = 0.1$ MPa} were obtained from Cannon Instruments, USA, with assigned lot number 5401 with a use-by date of November 11, 2007. The supplier measured the kinematic viscosity of S20 at temperatures between (293 and 373) K using long (at least 400 mm) capillary Master Viscometers according to ASTM D 2164. The supplier also provided density values at all temperatures measured in accordance with ASTM D 1480. The expanded uncertainty in the kinematic viscosity was ± 0.25 % relative to water, for which the uncertainty at $T = 298$ K and $p = 0.1$ MPa is ± 0.25 %, and the uncertainty in the density was ± 0.02 %. When these uncertainties are combined in quadrature, the expanded uncertainty in the dynamic viscosity is ± 0.35 % assuming that no additional uncertainty arises from the step-up procedure.[9] However, measurements of the viscosity of reference materials between different laboratories have been reported with discrepancies of less than ± 0.1 %.[10]

Prior to use in the falling sinker viscometer, certified viscosity material S20 was filtered through a glass sinter with a pore diameter of between (40 and 60) μm. S20 is probably a mixture of hydrocarbons, and the chemical composition of each batch was neither determined in this work nor disclosed by the supplier.

The supplier cited values of both density and viscosity at a pressure of 0.1 MPa and seven temperatures of (293.15, 298.15, 310.93, 313.15, 323.15, 372.04, and 373.15) K that are listed in Table 1. To obtain the viscosity and density at other experimental temperatures and to compare the values with those for the two other batches used in refs 6 and 7, the certified reference values were fit to empirical functions. The reference values of viscosity were represented by the rule reported by Vogel[43] of

$$\ln(\eta/\eta^\circ) = e + \frac{f}{g + (T/\text{K})} \tag{2}$$

where $\eta^\circ = 1$ mPa·s. The constants e, f, and g of eq 2 were obtained by a nonlinear adjustment with the results $e = -2.72136$, $f = 773.4$, and $g = -171.306$ and a standard deviation of $\sigma(\eta) = 0.0044$ mPa·s, which is about 0.3 % of

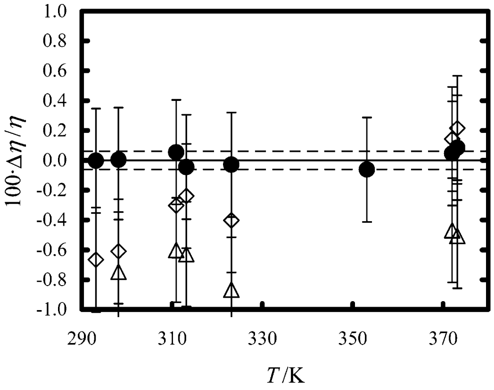

Figure 1. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the viscosity of η(exptl) provided by the supplier from η(calcd) of eq 2 for certified reference material S20. The dashed lines are $200\cdot\sigma(\eta)/<\eta> \approx 0.06$, and the factor of 2 is for the 0.95 confidence interval. The error bars are the estimated expanded uncertainty in $\delta\eta/\eta \approx 0.0035$ that includes the uncertainty in the viscosity of water at $T = 298$ K and $p = 0.1$ MPa and the density. ●, this batch from Table 1; △, certified values for the batch of S20 used in ref 6; and ◇, certified values for the batch of S20 used in ref 7.

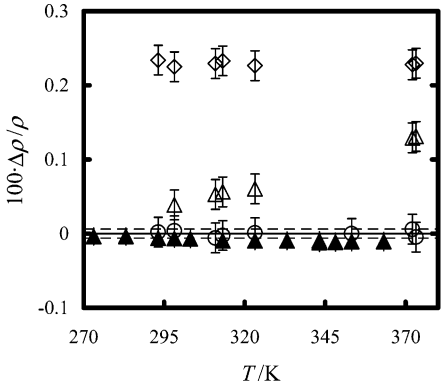

Figure 2. Fractional deviation $\Delta\rho/\rho = \{\rho(\text{exptl}) - \rho(\text{calcd})\}/\rho(\text{calcd})$ of the density of ρ(exptl) provided by the supplier from ρ(calcd) of eq 3 for certified reference material S20. The dashed lines are $200\cdot<|\delta\rho|>/<\rho> \approx 0.006$ where $<|\delta\rho|>$ is the average absolute deviation of the supplier's values from eq 3 and the error bars are the expanded uncertainty in the suppliers values and our measurements of ± 0.02 %. ○, manufacturer's certified values for this batch from Table 1; ▲, our measurements for this batch from Table 4; △, supplier's certified values for the batch of S20 used in ref 6; and ◇, supplier's certified values for the batch of S20 used in ref 7.

Table 2. Viscosity η Obtained from the Vibrating Wire Viscometer and Density ρ Obtained from the Vibrating Tube Densimeter (DMA 512) for Certified Reference Material S20 at Temperatures T and Pressures p with Expanded Uncertainties (Confidence Interval of 0.95)

T/K	p/MPa	ρ/kg·m^{-3}	η/mPa·s
298.150 ± 0.020	0.1		29.41 ± 0.62
298.150 ± 0.020	10.00 ± 0.50	866.7 ± 1.5	36.57 ± 0.87
298.150 ± 0.020	20.00 ± 0.50	872.3 ± 1.5	45.0 ± 1.1
298.150 ± 0.020	30.00 ± 0.50	877.1 ± 1.5	55.2 ± 1.3
298.150 ± 0.020	50.00 ± 0.50	886.4 ± 1.5	80.0 ± 1.8
313.150 ± 0.020	10.00 ± 0.50		18.77 ± 0.44
313.150 ± 0.020	20.00 ± 0.50		22.55 ± 0.52
313.150 ± 0.020	30.00 ± 0.50		26.97 ± 0.63
313.150 ± 0.020	50.00 ± 0.50		39.16 ± 0.91
313.150 ± 0.020	70.00 ± 0.50		54.5 ± 1.3
323.150 ± 0.020	0.1		10.79 ± 0.23
323.150 ± 0.020	10.00 ± 0.50	852.0 ± 1.5	12.86 ± 0.31
323.150 ± 0.020	20.00 ± 0.50	857.8 ± 1.5	15.41 ± 0.37
323.150 ± 0.020	30.00 ± 0.50	863.2 ± 1.5	18.60 ± 0.43
323.150 ± 0.020	50.00 ± 0.50	873.3 ± 1.5	26.01 ± 0.60
323.150 ± 0.020	70.00 ± 0.50	882.3 ± 1.5	35.13 ± 0.80
348.150 ± 0.020	0.10		5.10 ± 0.11
348.150 ± 0.020	10.00 ± 0.50	837.4 ± 1.5	6.07 ± 0.14
348.150 ± 0.020	20.00 ± 0.50	843.9 ± 1.5	7.12 ± 0.16
348.150 ± 0.020	30.00 ± 0.50	849.9 ± 1.5	8.42 ± 0.21
348.150 ± 0.020	50.00 ± 0.50	860.0 ± 1.5	11.40 ± 0.28
348.150 ± 0.020	70.00 ± 0.50	870.4 ± 1.5	15.14 ± 0.39
373.150 ± 0.020	0.10		3.038 ± 0.063
373.150 ± 0.020	10.00 ± 0.50	822.5 ± 1.5	3.542 ± 0.078
373.150 ± 0.020	20.00 ± 0.50	829.6 ± 1.5	4.086 ± 0.089
373.150 ± 0.020	30.00 ± 0.50	836.4 ± 1.5	4.73 ± 0.10
373.150 ± 0.020	50.00 ± 0.50	847.9 ± 1.5	6.20 ± 0.13
	70.00 ± 0.50	858.3 ± 1.5	8.00 ± 0.17
398.150 ± 0.020	0.10		2.012 ± 0.043
398.150 ± 0.020	10.00 ± 0.50	807.5 ± 1.5	2.282 ± 0.056
398.150 ± 0.020	20.00 ± 0.50	815.2 ± 1.5	2.644 ± 0.058
398.150 ± 0.020	30.00 ± 0.50	822.0 ± 1.5	2.994 ± 0.065
398.150 ± 0.020	50.00 ± 0.50	835.1 ± 1.5	3.885 ± 0.084
398.150 ± 0.020	70.00 ± 0.50	846.5 ± 1.5	4.89 ± 0.10
423.150 ± 0.020	0.10		1.402 ± 0.030
423.150 ± 0.020	10.00 ± 0.50	792.1 ± 1.5	1.596 ± 0.036
423.150 ± 0.020	20.00 ± 0.50	800.8 ± 1.5	1.813 ± 0.042
423.150 ± 0.020	30.00 ± 0.50	808.3 ± 1.5	2.039 ± 0.046
423.150 ± 0.020	50.00 ± 0.50	822.1 ± 1.5	2.586 ± 0.057
423.150 ± 0.020	70.00 ± 0.50	834.0 ± 1.5	3.247 ± 0.074

$<\eta>$ over the temperature range of (298 to 373) K. The relative difference of the reference values from eq 2 is shown in Figure 1 where the average deviation is 0.04 % and the maximum deviation is 0.08 %, which is at least a factor of 4.4 within the 0.35 % uncertainty cited by the supplier. The dashed lines in Figure 1 are $200\cdot\sigma(\eta)/<\eta> \approx 0.06$, and the factor of 2 is for the 0.95 confidence interval. The certified values of η for the batches of S20 used in refs 6 and 7 differ from the batch used in this work, as shown in Figure 1, by about the combined expanded uncertainty in the measurements of 0.7 %.

The densities listed in Table 1 were fit to

$$\rho/\text{kg}\cdot\text{m}^{-3} = h(T/\text{K}) + j \qquad (3)$$

and the parameters $h = -0.64306$ and $j = 1050.797$ were obtained to represent the cited values for the batch used in this work. The relative difference of the reference values from eq 3 are shown in Figure 2 where the maximum deviation is 0.006 %, a factor of about 3 less than the cited uncertainty, and the average absolute deviation is 0.003 %, both within the 0.02 % uncertainty cited by the supplier. The certified values of ρ for the batches of S20 used in refs 6 and 7 differ from the batch used in this work, as shown in Figure 2, by about 0.24 % for the batch used in ref 7 and between (0.04 and 0.13) % for the batch used in ref 6, which is up to 3.25 times the combined expanded uncertainty cited by the supplier. We conclude that interpolating to temperatures within the range of (293.15 to 373.15) K of the cited values with eqs 2 and 3 introduced a negligible additional uncertainty in the values of density and viscosity for this batch.

For the vibrating wire viscometer and high-pressure vibrating tube densimeter, measurements were performed at seven temperatures in the range of (298 to 423) K at pressures between (0.1 and 70) MPa, while for the falling sinker viscometer, measurements were performed at five temperatures from (293 to 333) K and pressures below 275 MPa.

Results and Discussion

The viscosity of S20 obtained with the vibrating wire viscometer is listed in Table 2 along with the density determined with a vibrating tube at temperatures between (298 and 423) K and pressure up to 70 MPa, while the viscosity obtained with the falling sinker viscometer is listed in Table 3, and the densities determined at $p \approx 0.1$ MPa with the other vibrating tube densimeter is given in Table 4. Small corrections have been

Table 3. Viscosity η Obtained with the Falling Sinker Viscometer of Diameter d for Certified Reference Material S20 at Temperatures T and Pressures p with Expanded Uncertainties (Confidence Interval of 0.95)

d/mm	T/K	p/MPa	η/mPa·s	T/K	p/MPa	η/mPa·s
6.0	273.150 ± 0.016	0.1	126.7 ± 2.9	313.150 ± 0.016	0.1	15.32 ± 0.35
	273.150 ± 0.016	0.1	126.7 ± 2.9	313.150 ± 0.016	0.8 ± 0.1	15.53 ± 0.35
	283.150 ± 0.016	0.1	66.0 ± 1.5	313.150 ± 0.016	20.5 ± 0.1	23.06 ± 0.52
	283.150 ± 0.016	0.1	66.0 ± 1.5	313.150 ± 0.016	40.1 ± 0.1	33.48 ± 0.76
	293.150 ± 0.016	0.1	37.66 ± 0.85	313.150 ± 0.016	60.3 ± 0.1	48.44 ± 1.1
	293.150 ± 0.016	0.9 ± 0.10	38.42 ± 0.87	313.150 ± 0.016	80.4 ± 0.1	68.9 ± 1.6
	293.150 ± 0.016	25.8 ± 0.10	67.8 ± 1.5	323.150 ± 0.016	0.1 ± 0.1	10.60 ± 0.24
	293.150 ± 0.016	50.7 ± 0.10	115.8 ± 2.6	323.150 ± 0.016	0.1 ± 0.1	10.76 ± 0.24
	293.150 ± 0.016	75.5 ± 0.10	192.3 ± 4.4	323.150 ± 0.016	0.7 ± 0.1	10.86 ± 0.25
	293.150 ± 0.016	75.6 ± 0.10	192.7 ± 4.4	323.150 ± 0.016	10.5 ± 0.1	13.11 ± 0.30
	293.150 ± 0.016	100.6 ± 0.10	314.8 ± 7.2	323.150 ± 0.016	25.6 ± 0.1	17.31 ± 0.39
	293.150 ± 0.016	125.6 ± 0.10	506 ± 11	323.150 ± 0.016	50.7 ± 0.1	26.83 ± 0.61
	293.150 ± 0.016	150.2 ± 0.10	796 ± 18	323.150 ± 0.016	75.7 ± 0.1	40.60 ± 0.92
		174.6 ± 0.10	1231 ± 28	323.150 ± 0.016	100.6 ± 0.1	60.3 ± 1.4
6.0	298.150 ± 0.016	0.1	29.24 ± 0.66	323.150 ± 0.016	125.6 ± 0.1	88.5 ± 2.0
	298.150 ± 0.016	0.7 ± 0.10	29.64 ± 0.67	323.150 ± 0.016	150.5 ± 0.1	128.2 ± 2.9
	298.150 ± 0.016	10.2 ± 0.10	36.71 ± 0.83	323.150 ± 0.016	175.4 ± 0.1	183.9 ± 4.2
	298.150 ± 0.016	25.7 ± 0.10	51.5 ± 1.2	323.150 ± 0.016	199.8 ± 0.1	259.6 ± 5.9
	298.150 ± 0.016	50.6 ± 0.10	86.3 ± 2.0	323.150 ± 0.016	249.4 ± 0.1	512 ± 12
	298.150 ± 0.016	75.5 ± 0.10	141.0 ± 3.2			
	298.150 ± 0.016	100.6 ± 0.10	226.6 ± 5.1			
	298.150 ± 0.016	125.9 ± 0.10	359.6 ± 8.1			
	298.150 ± 0.016	151.0 ± 0.10	561 ± 13			
	298.150 ± 0.016	175.3 ± 0.10	853 ± 19			
	298.150 ± 0.016	199.3 ± 0.10	1280 ± 29			
6.3	313.150 ± 0.016	0.1	15.42 ± 0.35	348.150 ± 0.016	0.1	5.25 ± 0.12
	313.150 ± 0.016	0.1	15.45 ± 0.35	348.150 ± 0.016	0.7 ± 0.1	5.41 ± 0.12
	323.150 ± 0.016	0.1	10.80 ± 0.24	348.150 ± 0.016	10.3 ± 0.1	6.34 ± 0.14
	323.150 ± 0.016	24.5 ± 0.10	17.04 ± 0.39	348.150 ± 0.016	25.7 ± 0.1	8.08 ± 0.18
	323.150 ± 0.016	48.8 ± 0.10	26.06 ± 0.59	348.150 ± 0.016	50.1 ± 0.1	11.63 ± 0.26
	323.150 ± 0.016	98.9 ± 0.10	59.0 ± 1.3	348.150 ± 0.016	75.5 ± 0.1	16.65 ± 0.38
	323.150 ± 0.016	151.6 ± 0.10	130.8 ± 3.0	348.150 ± 0.016	100.6 ± 0.1	23.35 ± 0.53
6.3	333.150 ± 0.016	0.1	7.86 ± 0.18	348.150 ± 0.016	125.5 ± 0.1	32.29 ± 0.73
	333.150 ± 0.016	0.1	7.86 ± 0.18	348.150 ± 0.016	150.6 ± 0.1	44.27 ± 1.0
	333.150 ± 0.016	0.5 ± 0.10	7.94 ± 0.18	348.150 ± 0.016	175.5 ± 0.1	60.1 ± 1.4
	333.150 ± 0.016	20.8 ± 0.10	11.38 ± 0.26	348.150 ± 0.016	200.1 ± 0.1	80.8 ± 1.8
	333.150 ± 0.016	40.6 ± 0.10	15.85 ± 0.36	348.150 ± 0.016	225.5 ± 0.1	108.6 ± 2.5
	333.150 ± 0.016	60.1 ± 0.10	21.63 ± 0.49	348.150 ± 0.016	250.1 ± 0.1	144.4 ± 3.3
	333.150 ± 0.016	80.6 ± 0.10	29.60 ± 0.67	348.150 ± 0.016	275.8 ± 0.1	193.8 ± 4.4

Table 4. Density ρ Obtained from the Vibrating Tube Densimeter (DMA 5000) for Certified Reference Material S20 at Temperatures T and p = 0.1 MPa with Expanded Uncertainties (Confidence Interval of 0.95)

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
273.15 ± 0.02	875.11 ± 0.11	333.15 ± 0.02	836.48 ± 0.10
283.15 ± 0.02	868.68 ± 0.11	343.15 ± 0.02	830.05 ± 0.10
293.15 ± 0.02	862.23 ± 0.10	343.15 ± 0.02	830.03 ± 0.10
298.15 ± 0.02	859.01 ± 0.10	348.15 ± 0.02	826.82 ± 0.10
303.15 ± 0.02	855.79 ± 0.10	353.15 ± 0.02	823.61 ± 0.10
313.15 ± 0.02	849.34 ± 0.10	363.15 ± 0.02	817.18 ± 0.10
323.15 ± 0.02	842.91 ± 0.10		

applied to the reported viscosity and density to reduce all values to the stated temperature for each isotherm. The uncertainties, listed in Tables 2 through 4, are at a confidence interval of 0.95 (k = 2) and were obtained by combining in quadrature uncertainties arising from the instrument with dη/dT and dη/dp for viscosity and dρ/dT with dρ/dp for density. For both viscosity and density, the major source of uncertainty (by at least a factor of 5) arises from the uncertainty of the viscometer and densimeter as described in the Apparatus and Experimental Procedure section where an expanded uncertainty of ≈± 2 % was assigned to the viscosity obtained from the vibrating wire, that is in part based on the work reported in refs 5 and 20, ± 2.3 % to the viscosity from the falling sinker, 0.2 % to the density from the vibrating tube operating at $p \leq 70$ MPa, and ± 0.05 % for densities determined with the $p \leq 1$ MPa vibrating tube. The next most significant and quantifiable contribution to the uncertainties arises from dη/dp for viscosity and dρ/dp for density. These derivatives were estimated from a combination of our results and the δp listed in the respective Tables 2 and 3. The contribution to $\delta\eta$ from δp is about 5 times greater at a given pressure for the vibrating wire than for the falling sinker reflecting the larger δp given for the pressure gauge used in the vibrating wire apparatus. For the vibrating wire viscometer, $\delta\eta$ from δp varies between (0.01 and 1.4) mPa·s {about (0.6 to 0.9) %} while for the falling sinker viscometer $\delta\eta$ from δp covered the range from (0.008 to 2.7) mPa·s {about (0.14 to 0.21) %}; the $\delta\eta$ decreased with increasing temperature at a pressure. The error δ from δp varied from (0.06 to 0.2) kg·m^{-3} {about (0.01 to 0.02) %}. The contribution to the uncertainty from either dη/dT or dρ/dT was estimated from a combination of our results and the δT listed in Table 4. The contribution to $\delta\eta$ from δT for the vibrating wire viscometer covered the range of −(0.0002 to 0.12) mPa·s {about −(0.01 to 0.03) %} while for the falling sinker the $\delta\eta$ lies between −(0.035 to −0.0014) mPa·s {about −(0.04 to 0.02) %} and the contribution to $\delta\rho \approx -0.006$ kg·m^{-3} (about 0.0008 %). For our measurements the uncertainty with which the pressure is measured is of higher significance than the uncertainty of temperature. The required derivatives were determined from an analysis of the results. In the absence of a chemical analysis for S20, the contribution to the uncertainty arising from the uncertainty in composition was assumed to be 0. The η obtained with the (6 and 6.3) mm diameter sinkers can be compared at five overlapping temperatures and pressures with the result $100\cdot|\delta\langle\eta\rangle|/\langle\eta\rangle \approx 1.4$, which is within the expanded uncertainty of either measurement. The values obtained from the 6.0 mm sinker lie between −1.9 % where $\langle\eta\rangle$(323 K, 0.1 MPa) = 10.7 mPa·s and 2.9 % where

$<\eta>$(323 K, 50 MPa) = 26.4 mPa·s from determined with the 6.3 mm sinker; here $<\eta>$ is the mean of the values obtained with the (6.0 and 6.3) mm diameter sinkers at a temperature and pressure. The maximum difference is within 1.3 times the expanded uncertainty of a measurement and within the combined uncertainty of both. The η obtained from the vibrating wire and falling sinker viscometers can be compared at 7 η between (5 and 86) mPa·s for the 6.0 mm sinker and at 4 η between (5 and 12) mPa·s for the 6.3 mm sinker. For the 6.0 mm sinker, $100 \cdot |\delta<\eta>|/<\eta> \approx 1.3$ with a maximum difference of −3.1 % at $<\eta>$(323 K, 50 MPa) = 26.8 mPa·s and a minimum of 0.6 % at η(298 K, 0.1 MPa) = 29.5 mPa·s. For the 6.3 mm sinker $100 \cdot |\delta<\eta>|/<\eta> \approx 2.8$ with a maximum difference of −4.2 % at $<\eta>$(348 K, 10 MPa) = 6.2 mPa·s a minimum of −2 % at η(348 K, 50 MPa) = 6.3 mPa·s. All these differences are within the combined expanded uncertainty of the falling sinker and vibrating wire viscometers. Nevertheless, the agreement in viscosity obtained from two experimental techniques that utilize different principles, and thus suffer from quite different sources of systematic error, is considered remarkable.

For a tungsten wire with $\rho_s = 19300$ kg·m^{-3} tensioned between two rigid clamps so that $f_0 = 1.2$ kHz, we have estimated, from eqs 3 through 9 of ref 20, the maximum measurable viscosity for a wire with $R = 0.075$ mm, assuming this is given by $Q = 2$, with the result $\eta < 200$ mPa·s. These conditions adhere to the experimental requirement of a frequency range of at least 5*g*. Thus, the greatest $\eta \approx 80$ mPa·s measured with this instrument is only 0.4 of the maximum operating value for this *R* wire. To verify the validity of these calculations, we also estimated the *Q* as a function of η at $f = 1.2$ kHz for $R \approx 0.075$ mm as used by Kandil et al.[20] and $R = 0.05$ mm used by Lundstrom et al.[6] Our estimates differed from the measured values by less than ± 10 % and if we take this as a bound on the upper measurable viscosity for a wire with $R = 0.075$ mm of about 200 mPa·s for an assumed minimal measurable $Q = 2$. However, useful values of viscosity can be obtained for $Q < 2$ as demonstrated in refs 6 and 20.

The densities ρ(*T*, 0.1 MPa) obtained from the low-pressure vibrating tube densimeter (DMA 5000), listed in Table 4, all lie below eq 3, as shown in Figure 2, by between (0.004 and 0.01) kg·m^{-3}, within the assigned expanded uncertainty of 0.05 kg·m^{-3}.

To represent the densities $\rho(T, p)$ of Table 2 obtained with the high-pressure vibrating tube densimeter (DMA 512), the modified Tait equation[36] was used with the form

$$\{\rho(T, p) - \rho_r(T, p_r)\}/\rho(T, p) = C \ln\{(B(T) + p)/(B(T) + p_r)\} \tag{4}$$

where $B(T)$ is given by

$$B(T) = A_0 + A_1 T + A_2 T^2 \tag{5}$$

In eq 4, $p_r = 0.1$ MPa and $\rho_r(p_r)$ is the density of the certified reference material cited by the supplier and represented by eq 3. The $\rho_r(p_r)$ values were combined with the density values obtained with the vibrating tube from Table 2 to determine the adjustable parameters C, A_0, A_1, and A_2. In this case we did not constrain $C = 0.21$ as reported by Dymond and co-workers[44−46] for hydrocarbons and as we did in ref 20. The coefficients so determined are $C = 0.0515376$, $A_0 = 257.23505$ MPa, $A_1 = -0.951082$ MPa·K^{-1}, and $A_2 = 0.00096403$ MPa·K^{-2} together with the standard deviation $\sigma(\rho) = 0.74$ kg·m^{-3} (about 0.086%).

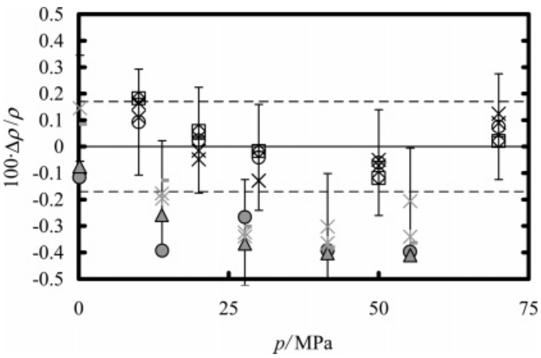

Figure 3. Fractional deviation $\Delta\rho/\rho = \{\rho(\text{exptl}) - \rho(\text{calcd})\}/\rho(\text{calcd})$ of the density in Table 2 ρ(exptl) from ρ(calcd) obtained from a combination of eqs 4 and 5 with coefficients given in the text for certified reference material S20. The dashed line is the expanded uncertainty of the fit of ± 0.17 %: ○, *T* = 298 K; ◇, *T* = 323 K; □, *T* = 348 K; +, *T* = 373 K; ∗, *T* = 398 K; ×, *T* = 423 K; gray filled circle, ref 6, *T* = 298 K; gray filled triangle, ref 6, *T* = 313 K; −, ref 6, *T* = 333 K; gray times sign, ref 6, *T* = 353 K; gray asterisk, ref 6, *T* = 393 K.

The densities from Table 2 are shown relative to the smoothing eqs 4 and 5 in Figure 3 for certified reference material S20. The dashed lines are $2 \cdot \sigma(\rho)$, the expanded uncertainty of eqs 4 and 5. For the sake of clarity the expanded uncertainties of the measurements are shown, in Figure 3, with error bars solely for the results obtained at $T = 298$ K. The densities obtained for S20 deviate from eqs 4 and 5 by less than ± 0.2 % and are within the expanded uncertainty of our measurements (about 0.2 %). The densities reported by Lundstrom et al.[6] for a different batch, also shown in Figure 3, differ from eqs 4 and 5 by between −(0.1 and 0.4) % and agree with the correlation for the batch used for this work within the combined expanded uncertainty of this correlation and their measurements.

The density is required to obtain viscosity from both the vibrating wire and falling sinker viscometers. For the vibrating wire viscometer the density was obtained with precision sufficient for this purpose from eqs 4 and 5. For the falling sinker viscometer the density was estimated from a combination of the measurements listed in Tables 2 and 4 with the procedure outlined here and reported elsewhere.[38] The densities in Table 4 were represented by eq 3 with $h = -0.643756$ and $j = 1050.95$. The measurements listed in Table 2 were used to estimate the isothermal compressibility, defined by $\kappa_T = -V^{-1}(\partial V/\partial p)_T$, from the linear secant given by

$$\kappa_T = -\frac{V(T, p_{\text{ref}}) - V(T, p)}{V(T, p_{\text{ref}})(p - p_{\text{ref}})} \tag{6}$$

at each experimental temperature *T* and pressure *p*. In eq 6 $V(T, p_{\text{ref}}) = \rho^{-1}$ and $p_{\text{ref}} = 0.1$ MPa at a temperature *T*. The κ_T^{-1} so obtained were fit to a Hayward-type equation[36,47] of the form

$$\kappa_T^{-1}/\text{MPa} = [\alpha_{00} + \alpha_{10}(\text{K}/T)] + [\alpha_{01} + \alpha_{11}(\text{K}/T)](p/\text{MPa}) \tag{7}$$

and the parameters $\alpha_{00} = -3472.74$, $\alpha_{10} = 1.65689 \cdot 10^6$, $\alpha_{01} = 32.1079$, and $\alpha_{11} = -9716.82$ were determined. At the temperatures and pressure for which the falling sinker viscometer was operated, the $\rho(T, p)$ were estimated from a combination of the densities listed in Table 4 at $p = 0.1$ MPa and eqs 6 and 7. Because the fluid density enters the working equation for the falling sinker viscometer through the buoyancy factor $(1 - \rho/\rho_s)$ and $\rho_s \approx 9.5 \cdot \rho$ to obtain $\delta\eta < 1$ % requires ρ be known within < 5 %. The ρ obtained from eqs 6 and 7 differ from the values listed in Table 2 by less than ± 0.1 %. The falling sinker

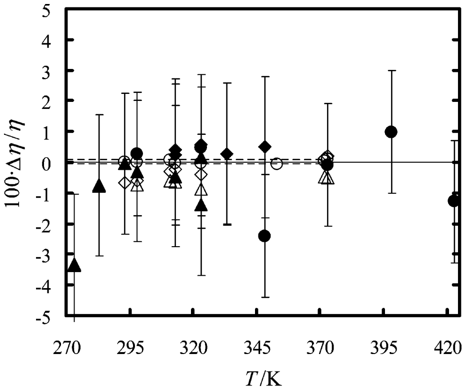

Figure 4. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the viscosity of η(exptl) at $p = 0.1$ MPa provided by the supplier from η(calcd) of eq 2 for certified reference material S20. The dashed lines are $200 \cdot \sigma(\eta)/<\eta> \approx 0.06$, and the factor of 2 is for the 0.95 confidence interval and the error bars are the estimated expanded uncertainty in our measurements. ●, this batch from Table 2 obtained with the vibrating wire; ▲, this batch from Table 3 obtained with the falling sinker of diameter 6.0 mm; ◆, this batch from Table 3 obtained with the falling sinker of diameter 6.3 mm; ○, certified values for this batch; △, certified values for the batch of S20 used in ref 6; and ◇, certified values for the batch of S20 used in ref 7.

viscometer was operated at a maximum pressure of 275 MPa that is a pressure of 205 MPa above the maximum pressure at which the density was measured of 70 MPa. At these pressures the density was obtained from eq 7. The uncertainty in the densities so determined was estimated to be of the order of < ± 1 %. The estimated uncertainty is based on both comparing the density of methylbenzene obtained from an extrapolation over a similar pressure range with experimental values and the results reported previously. This estimated uncertainty in density does not introduce any additional uncertainty to the viscosity obtained from the falling sinker.

The viscosity obtained at $p = 0.1$ MPa from both vibrating wire and falling sinker viscometers is shown as deviations from eq 2 in Figure 4 along with the supplier's cited values and those reported in refs 6 and 7. The dashed lines are $2 \cdot \sigma(\rho)$ the expanded uncertainty of eq 2 and the expanded uncertainties of the results obtained with the vibrating wire and both sinkers are shown with bars in Figure 4. The viscosities obtained for S20 at $p = 0.1$ MPa deviate from eq 2 by between −3.5 % for the 6.0 mm sinker at $T = 273$ K and 1 % for the vibrating wire at $T = 398$ K, and these differences are within a multiple of 1.3 times the expanded uncertainty assigned to these measurements of about 2 %. The vibrating wire result lies 1.3 % below eq 2 at $T = 423$ K, which is an extrapolation to a temperature 50 K above the maximum used to obtain the coefficients of eq 2 from the supplier's cited values for the batch used in this work. The viscosities cited by the supplier for the batches used by Lundstrom et al.[6] and Sopkow et al.[7] are also shown in Figure 4, and they differ from eq 2 by between (−0.86 and 0.21) %. The former is about 2.5 times the estimated expanded uncertainty of the supplier's values. Plausible sources for these observed, albeit small (< 1 %), variations in viscosity between batches at $p = 0.1$ MPa might arise from either contamination of the sample during the measurements or variations in the chemical composition of each batch of S20. No measurements were performed to determine the source of these differences.

There are numerous models, some with theoretical basis, that have been used to represent the viscosity of liquids and, excluding that reported by Allal et al.,[48,49] have been reviewed in ref 50. One method in ref 50 uses a semiempirical equation based on the hard-sphere theory of transport properties in dense fluids. This scheme was developed and applied successfully by Assael et al.[39] for *n*-alkanes[51] and their mixtures,[52] for aromatic hydrocarbons,[53] and by others for refrigerants.[54,55]

Unfortunately, in the absence of a chemical composition for each certified reference material and therefore knowledge of both the molar mass and also then the characteristic molar volume, we were unable to utilize the method of ref 50 or that reported in refs 48 and 49. Other methods that are similarly constrained and thus precluded have been reported by Huber et al.[56] Therefore, to correlate the measured $\eta(T, p)$ of the certified reference material, an empirical method was required. The following methods were chosen arbitrarily for evaluation: (1) modification of eq 2 to include p as used by Harris et al.[38] for the viscosity of ionic liquids with six adjustable parameters; (2) the empirical function recommended by Litovitz[57] for the temperature dependence of viscosity modified to accommodate pressure as described by Harris et al.[38] that has five adjustable parameters; and (3) the empirical expression used in ref 6 also with five adjustable parameters. Empirical expression of method (1) is

$$\eta(T, p)/\eta^\circ = \exp\{a' + b'(p/\text{MPa}) + (c' + d'(p/\text{MPa}) + e'(p/\text{MPa})^2)/[(T/\text{K}) + T_0]\} \quad (8)$$

where a', b', c', d', e', and T_0 are adjustable parameters while the functional form of method (2) is

$$\eta(T, p)/\eta^\circ = \exp[a + b(p/\text{MPa}) + (c + d(p/\text{MPa}) + e(p/\text{MPa})^2)/(T/\text{K})^3] \quad (9)$$

where a, b, c, d, and e are adjustable parameters. Method (3) had the form

$$\eta(T, p)/\eta^\circ = \exp\left\{\begin{matrix} \exp\left[k + \dfrac{l}{m + (T/\text{K})}\right]\dfrac{(p - p_r)}{p^\circ} \\ + [n + q(T/\text{K})][(p - p_r)]^2 \end{matrix}\right\} \quad (10)$$

where k, l, m, n, and q are adjusted to best represent the results, $p_r = 0.1$ MPa, and $p^\circ = 1$ MPa. In eqs 8 to 10, $\eta^\circ = 1$ mPa·s. Methods (1) through (3) were each able to represent the measurements obtained with both the vibrating wire and falling sinker viscometers and, perhaps because of the one additional adjustable parameter, method (1) based on the standard deviation of the fit gave a marginally better representation of the results. The coefficients of eq 8 obtained from the regression to the viscosities of Tables 2 and 3 are $a' = -2.633280$, $b' = 7.291157 \cdot 10^{-4}$, $c' = 756.9913$, $d' = 2.654074$, $e' = -1.816725 \cdot 10^{-3}$, and $T_0 = -172.1248$. The viscosities from Tables 2 and 3 are shown relative to eq 8 with these coefficients in Figure 5 where the dashed lines represent $200 \cdot \sigma(\eta)/<\eta> = 2.3$, where $\sigma(\eta)$ is the standard deviation of the fit, and $<\eta>$ is the average measured viscosity of ≈ 93 mPa·s. Unfortunately, the viscosities obtained with the falling sinker deviate from eq 8 with a systematic undulation that suggests either a systematic error or the functional form of eq 8 is not completely satisfactory. However, when this falling sinker viscometer was used to determine the viscosity of other fluids, no systematic errors were observed.[24,38] Consequently, an additional term $g'p^2$ was included in eq 8 to give

$$\eta(T, p)/\eta^\circ = \exp\left\{\begin{matrix} a' + b'(p/\text{MPa}) + g'(p/\text{MPa})^2 \\ + (c' + d'(p/\text{MPa}) + e'(p/\text{MPa})^2)/[(T/\text{K}) + T_0] \end{matrix}\right\} \quad (11)$$

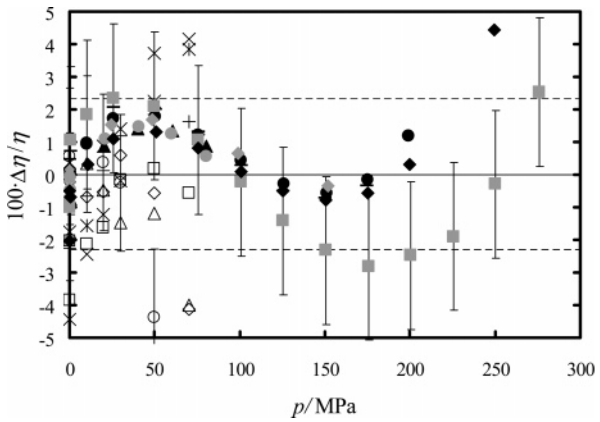

Figure 5. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta$ (calcd) of the viscosity of either Table 2 or Table 3 η(exptl) from the value obtained from eq 8 η(calcd) for certified reference material S20. The dashed lines are the expanded uncertainty of the fit of 2.3 %. ○, $T = 298$ K obtained from the vibrating wire viscometer; △, $T = 313$ K obtained from the vibrating wire viscometer; ◇, $T = 323$ K obtained from the vibrating wire viscometer; □, $T = 348$ K obtained from the vibrating wire viscometer; +, $T = 373$ K obtained from the vibrating wire viscometer; *, $T = 398$ K obtained from the vibrating wire viscometer; ×, $T = 423$ K obtained from the vibrating wire viscometer; gray filled box, $T = 273$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; gray filled diamond, $T = 283$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ■, $T = 293$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ●, $T = 298$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ▲, $T = 313$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ◆, $T = 323$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; gray triangle, $T = 313$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray diamond, $T = 323$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray circle, $T = 333$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray box, $T = 348$ K obtained with the falling sinker viscometer with $d = 6.3$ mm.

with no significant improvement in either the overall representation of the results or the systematic undulation. Nevertheless, the agreement between the results obtained from different techniques is considered remarkable and the $200\cdot(\eta)/\langle\eta\rangle = 2.3$ is equivalent to the estimated expanded uncertainty in our measurements. For the sake of clarity, error bars are only shown in Figure 5 for the falling sinker results at $T = 348$ K and the vibrating wire at $T = 298$ K.

The only measurements of viscosity as a function of pressure, of which we are aware, for S20 are those reported by Lundstrom et al.[6] and Sopkow et al.[7] that are shown in Figure 6 as deviations from eq 8 along with the values reported here in the overlapping temperature and pressure range. All but one of the measurements from refs 6 and 7 deviate from eq 8 by $< \pm 4.5$ %, which is within the combined estimated expanded uncertainty of the measurements reported here and in refs 6 and 7. The measurement reported by Lundstrom et al.,[6] $\langle\eta\rangle$(298 K, 41 MPa) = 75.88 mPa·s, lies 7.9 % above eq 8 about 2 times the combined uncertainty in these measurements and of ref 6. The value $\langle\eta\rangle$(298 K, 41 MPa) = 75.88 mPa·s was obtained from the weighted mean of η(298 K, 41 MPa) = 76.6 mPa·s obtained from a vibrating wire viscometer with $R \approx 0.05$ mm and η(298 K, 41 MPa) = 73.4 mPa·s determined with a commercially available oscillating sinker viscometer. The result η(298 K, 41 MPa) = 73.4 mPa·s determined with the oscillating sinker viscometer is 4.3 % above eq 8 and is equivalent to the difference observed for other measurements. However, the sinker used by Lundstrom et al.[6] was used outside the range of (2 to 50) mPa·s recommended by the manufacturer of the oscillating sinker viscometer. In ref 6 the uncertainty of operating the viscometer outside the range of the sinker was quantified with measurements on certified reference fluid for viscosity N35 that gave 62.45 mPa·s, which is 7.45 % above an interpolation of the manufacturer's cited values of $\eta = 58.12$ mPa·s. This discrepancy is greater than the difference of 4.3 % between the η obtained with the oscillating sinker in ref 6 and eq 8. A plausible source for the η(298 K, 41 MPa) = 76.6 mPa·s reported in ref 6 from the vibrating wire, which is greater than the estimate obtained from eq 8 by 8.9 %, might arise from operating the vibrating wire with a resonance quality factor of about 1.9.[6] No independent experiments have been performed to verify this conjecture. It is also entirely plausible the viscosity reported in ref 6 for S20 at $T = 298$ K and $p = 41$ MPa (from measurements with a sinker operated outside its range and a low-Q resonance of the vibrating wire) is both questionable and has, at least, a greater uncertainty than the 1.8 % assigned it in ref 6. Nevertheless, we conclude that S20 can serve as an adequate calibrant of instruments intended to measure the viscosity of reservoir hydrocarbons with an uncertainty of less than ± 10 %.

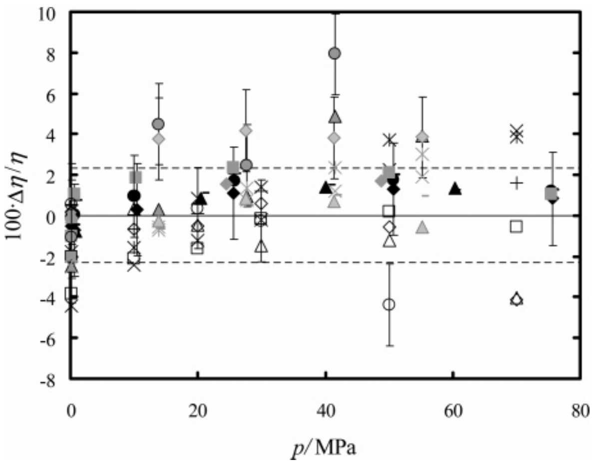

Figure 6. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the viscosity in either Table 2 or Table 3 η(exptl) from the value obtained from eq 8 η(calcd) for certified reference material S20. The dashed lines are the expanded uncertainty of the fit of 2.3 %. ○, $T = 298$ K obtained from the vibrating wire viscometer; △, $T = 313$ K obtained from the vibrating wire viscometer; ◇, $T = 323$ K obtained from the vibrating wire viscometer; □, $T = 348$ K obtained from the vibrating wire viscometer; +, $T = 373$ K obtained from the vibrating wire viscometer; ∗, $T = 398$ K obtained from the vibrating wire viscometer; ×, $T = 423$ K obtained from the vibrating wire viscometer; gray filled box, $T = 273$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; gray filled diamond, $T = 283$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ■, $T = 293$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ●, $T = 298$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ▲, $T = 313$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; ◆, $T = 323$ K obtained with the falling sinker viscometer with $d = 6.0$ mm; gray triangle, $T = 313$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray diamond, $T = 323$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray circle, $T = 333$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray box, $T = 348$ K obtained with the falling sinker viscometer with $d = 6.3$ mm; gray filled circle, ref 6 $T = 298$ K; gray filled triangle, ref 6, $T = 313$ K; −, ref 6, $T = 333$ K; gray times sign, ref 6, $T = 353$ K; gray asterisk, ref 6, $T = 393$ K; gray triangle, ref 7, $T = 313$ K; gray diamond, ref 7, $T = 353$ K.

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